Regioselective Construction of Substituted Conjugated Dienes Using an Olefin Cross-Metathesis Protocol

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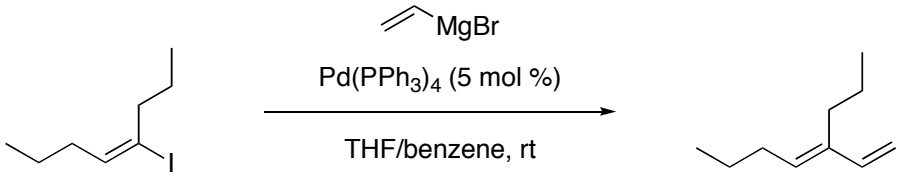
General Experimental Section. NMR spectra were recorded on an Oxford 300 MHz NMR spectrometer running Varian VNMR software. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), and broad (br). Spectroscopic data is provided for the major olefin isomer. For all vinylboronates reported the ^{13}C peak of the α-carbon is not observed due to the large quadrupolar effect of the attached boron nucleus. E/Z ratios given for the products indicate the ratios of the C=C bond formed in cross-metathesis and were determined from coupling constants of vinylic protons in the ^{1}H NMR spectrum.

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed with standard potassium permanganate stains or UV light. Flash column chromatography was performed using silica gel 60 (230-400 mesh). All glassware was either oven dried or flame dried, and reactions were done under an atmosphere of argon. All commercial chemicals were used as obtained except 1,4-diacetoxy-*cis*-2-butene,

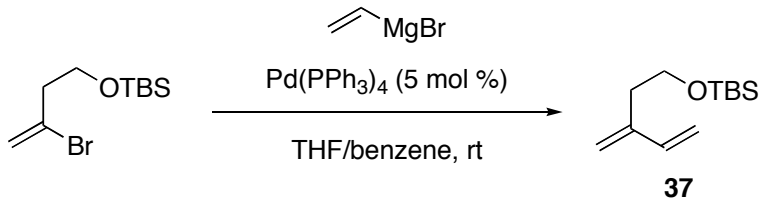
which was distilled from CaH_2. 3-Methyl-1,3-pentadiene was received (Aldrich) as a 70:30 mixture of E/Z isomers, and both isomers underwent cross-metathesis in the examples below (NMR spectral data is given for both isomers whenever it could be determined). Benzene and methylene chloride were dried by passage through solvent columns containing activated alumina. (*2Z,4E*)-2-Bromo-ethyl-sorbate[i] (**9**) (which was isolated and used as a 9:1 mixture of (*2Z,4E*)-2-bromo-ethyl-sorbate and (*2E,4E*)-2-bromo-ethyl-sorbate), 1,1-dibromo-1,3-pentadiene[ii] (**15**), and 2-hexylbuta-1,3-diene[iii] (**36**) were prepared according to literature procedures. Non-commercially available conjugated dienes were prepared as follows:



29

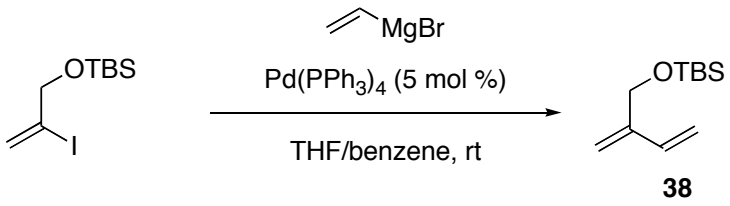
Diene 29. To a solution of $Pd(PPh_3)_4$ (340 mg, 0.29 mmol) in 30 mL benzene at rt was added (*E*)-4-iodo-4-octene[iv] (1.4 g, 5.9 mmol) and vinylmagnesium bromide (1M in THF, 11.8 mL, 11.8 mmol). After 3 h, saturated aqueous NH_4Cl was added and the mixture was extracted with 3 × 25 mL Et_2O. The organics were combined, washed with saturated aqueous $NaHCO_3$, water, brine, dried over $MgSO_4$, and concentrated. The crude oil was purified by flash chromatography (hexanes) to give 0.52 g (64%) **29** as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.68 (dd, J = 17.6, 11.0 Hz, 1H), 5.38 (t, J = 7.4 Hz, 1H), 5.21 (d, J = 17.9 Hz, 1H), 5.06 (dt, J = 11.0, 1.6 Hz, 1H), 2.11-2.19 (m, 4H), 1.34-1.57 (m, 4H), 0.91 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz,

$CDCl_3$, ppm): δ 136.6, 133.2, 130.9, 113.0, 35.7, 29.6, 23.3, 22.1, 14.2, 14.0. HRMS (EI) calc. for $C_{10}H_{18}$: 138.1409, found 138.1406.



37

Diene 37. Following the same procedure as **29**, 3-bromo-3-buten-1-ol *t*-butyldimethylsilyl ether[v] (1.0 g, 3.8 mmol), vinylmagnesium bromide (1M in THF, 7.5 mL, 7.5 mmol), and $Pd(PPh_3)_4$ (218 mg, 0.19 mmol) in 20 mL benzene gave 0.61 g (76%) of **37** as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.36 (dd, J = 17.6, 11.3 Hz, 1H), 5.24 (d, J = 17.6 Hz, 1H), 5.06 (d, J = 11.0 Hz, 1H), 5.06 (broad s, 1H), 5.03 (broad s, 1H), 3.74 (t, J = 7.1Hz, 2H), 2.46 (t, J = 7.1 Hz, 2H), 0.90 (s, 9H) 0.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.4, 139.1, 117.6, 113.5, 62.6, 35.2, 26.1, 18.6, -5.0. HRMS (EI) calc. for $C_{12}H_{24}OSi$: 212.1597, found 212.1592.



38

Diene 38. Following the same procedure as **29**, 1-(*t*-butyldimethylsiloxy)-2-iodopropene[iv,vi] (1.3 g, 4.4 mmol), vinylmagnesium bromide (1M in THF, 8.7 mL, 8.7 mmol), and $Pd(PPh_3)_4$ (252 mg, 0.22 mmol) in 23 mL benzene gave 0.24 g (28%) of **38** as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.39 (dd, J = 17.9, 11.0 Hz, 1H), 5.33 (br s, 1H), 5.17 (d, J = 18.1 Hz, 1H), 5.11 (br s, 1H), 5.04 (d, J = 11.0 Hz, 1H), 4.35 (t, J = 1.5 Hz, 2H), 0.93 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 145.1, 136.8, 114.9, 113.2, 62.6, 26.1, 18.6, -5.2. HRMS (EI) calc. for $C_{11}H_{22}OSi$: 198.1440, found 198.1449.

General Procedure for Cross-Metathesis Reactions with (*2Z,*4E)-2-Bromo-ethyl-sorbate and 1,1-Dibromo-1,3-pentadiene (Table 1). Entry 1, (2*Z*,4*E*)-ethyl 2-bromoundeca-2,4-dienoate (16). To a solution of catalyst **3** (20 mg, 0.023 mmol) in 2.3 mL CH_2Cl_2 was added (*2Z,*4E)-2-bromo-ethyl-sorbate (**9**) (100 mg, 0.46 mmol) and allylbenzene (**10**) (162 mg, 1.4 mmol), and the solution stirred for 12 h at 40 °C. The volatiles were removed by rotary evaporation, and the residue was purified by flash chromatography to give 92 mg (68%, 8.5:1 E/Z) **16** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.70 (d, J = 10.5 Hz, 1H), 7.21-7.39 (m, 5H), 6.56-6.64 (m, 1H), 6.47 (dt, J = 15.5, 6.7 Hz, 1H), 4.32 (q, J = 7.0 Hz, 2H), 3.59 (d, J = 6.7 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.0, 145.0, 140.92, 138.4, 128.6, 128.5, 128.4, 126.5, 113.2, 62.3, 39.7, 14.2. GC-MS (EI): 296 (M^+), 294 (M^+), 215, 169, 141.

Entry 2, (2*Z*,4*E*)-ethyl 2-bromo-5-phenylpenta-2,4-dienoate (17).[i] Following the general procedure for **16**, **9** (73 mg, 0.33 mmol), styrene (**11**) (104 mg, 1.0 mmol), and **3**

(30 mg, 0.033 mmol) in 1.8 mL CH_2Cl_2 gave 60 mg (65%, 10:1 E/Z) of **17** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.86 (d, J = 10.0 Hz, 1H), 7.55-7.58 (m, 2H), 7.38-7.41 (m, 3H), 7.07-7.25 (m, 2H), 4.35 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 162.9, 142.6, 141.1, 135.9, 129.5, 128.8, 127.5, 125.2, 114.3, 62.4, 14.2.

Entry 3, (2*Z*,4*E*)-ethyl 6-acetoxy-2-bromohexa-2,4-dienoate (18). Following the general procedure for **16**, **9** (132 mg, 0.60 mmol), 1,4-diacetoxy-*cis*-2-butene (**12**) (311 mg, 1.80 mmol), and **3** (51 mg, 0.060 mmol) in 3 mL CH_2Cl_2 gave 117 mg (70%, 7.5:1 E/Z) of **18** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.63 (d, J = 10.6 Hz, 1H), 6.67 (ddt, J = 15.5, 10.7, 1.7 Hz, 1H), 6.29-6.38 (ddt, J = 15.5, 5.6, 0.9 Hz, 1H), 4.73 (dd, J = 5.6, 1.5 Hz, 2H), 4.32 (q, J = 7.0 Hz, 2H), 2.14 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170.5, 163.7, 139.7, 137.9, 129.4, 115.7, 63.8, 62.9, 20.8, 14.1. GC-MS (EI): 278 (M^+), 276 (M^+), 215, 169, 141.

Entry 4, (2*Z*,4*E*)-ethyl 2-bromo-6-chlorohexa-2,4-dienoate (19). Following the general procedure for **16**, **9** (92 mg, 0.42 mmol), 1,4-dichloro-*cis*-2-butene (**13**) (105 mg, 0.84 mmol), and **3** (18 mg, 0.021 mmol) in 2 mL CH_2Cl_2 gave 51 mg (48%, 6:1 E/Z) of **19** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.64 (d, J = 10.5 Hz, 1H), 6.72 (dd, J = 15.5, 10.5 Hz, 1H), 6.56 (dt, J = 15.5, 7.2 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.17 (d, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 162.4, 139.1, 138.5, 130.3, 116.3, 62.7, 47.3, 14.3.

Entry 6, (*E*)-methyl 5,5-dibromopenta-2,4-dienoate (20). Following the general procedure for **16**, **15** (150 mg, 0.66 mmol), methyl acrylate (**14**) (114 mg, 1.33 mmol), and **3** (28 mg, 0.033 mmol) in 3.3 mL CH_2Cl_2 gave 70 mg (39%, >20:1 E/Z) of **20** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.16 (dd, J = 16.6, 12.8 Hz, 1H), 6.84 (d, 12.8 Hz, 1H), 5.90 (d, 16.6 Hz, 1H), 3.61 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.9, 140.1, 135.1, 124.1, 100.7, 52.3. HRMS (EI) calc. for $C_6H_6Br_2O_2$: 269.8735, found 269.8725.

Entry 7, (*E*)-1-(4,4-dibromobuta-1,3-dienyl)benzene (21). Following the general procedure for **16**, **15** (150 mg, 0.66 mmol), styrene (**11**) (138 mg, 1.33 mmol), and **3** (28 mg, 0.033 mmol) in 3.3 mL CH_2Cl_2 gave 115 mg (60%, >20:1 E/Z) of **21** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.44-7.47 (m, 2H), 7.25-7.38 (m, 3H), 7.10 (d, J = 8.9 Hz, 1H), 6.68-6.84 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 137.0, 136.2, 135.6, 128.7, 128.5, 126.7, 125.2, 91.3. HRMS (EI) calc. for $C_{10}H_8Br_2$: 287.8972, found 287.8981.

Entry 8, (*E*)-8,8-dibromoocta-5,7-dienyl acetate (22). Following the general procedure for **16**, **15** (150 mg, 0.66 mmol), 5-hexenyl acetate (**5**) (189 mg, 1.33 mmol), and **3** (28 mg, 0.033 mmol) in 3.3 mL CH_2Cl_2 gave 122 mg (56%, 5:1 E/Z ratio) of **22** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.86 (d, J = 10.0 Hz, 1H), 6.05 (ddt, J = 15.2, 10.0, 2.6 Hz, 1H), 5.85 (dt, J = 15.2, 7.0 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 2.06-2.15 (m, 2H), 2.00 (s, 3H), 1.55-1.65 (m, 2H), 1.39-1.50 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$,

ppm): δ 171.0, 138.5, 136.8, 127.5, 88.7, 64.1, 32.6, 28.0, 25.0, 20.9. HRMS (EI) calc. for $C_{10}H_{14}Br_2O_2$: 325.9361, found 325.9346.

General Procedure for Cross-Metathesis Reactions Using 1,2-Disubstituted 1,3-Butadienes (Table 2). Entry 1, 4,4,5,5-Tetramethyl-2-((1*E*,3*E*)-3-methylpenta-1,3-dienyl)-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-((1*E*,3*Z*)-3-methylpenta-1,3-dienyl)-1,3,2-dioxaborolane (30). To a solution of **3** (14 mg, 0.016 mmol) in CH_2Cl_2 (1 mL) was added 3-methyl-1,3-pentadiene (**28**) (27 mg, 0.32 mmol) and vinylboronate **23** (50 mg, 0.32 mmol). The solution stirred at 40 °C for 12 h, and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (5% ethyl acetate:hexanes) to give 54 mg (80%, >20:1 E/Z) of the two isomers of **30**. A small amount (10%) of the cross product missing the terminal methyl group (**25**) was identified by a broad singlet at 5.15 ppm in the ^{1}H NMR spectrum (terminal C=CH_2) and by HRMS (EI) (calc. for $C_{11}H_{19}BO_2$: 194.1478, found 194.1485). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.47 (d, J = 18.1 Hz, 1H, *Z*-isomer), 7.03 (d, J = 18.1 Hz, 1H, *E*-isomer), 5.76 (q, J = 6.8 Hz, 1H, *E*-isomer), 5.62 (m, 1H, *Z*-isomer), 5.55 (d, J = 18.1 Hz, 1H, *Z*-isomer), 5.42 (d, J = 18.1 Hz, 1H, *E*-isomer), 1.78 (d, J = 11.0 Hz, 3H), 1.73 (s, 3H), 1.26 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) of *E*-isomer: δ 154.7, 131.9, 129.1, 83.2, 25.0, 14.5, 11.5. HRMS (EI) calc. for $C_{12}H_{21}BO_2$ (for both isomers): 208.1635, found 208.1636 and 208.1627.

Entry 2, (2*E*,4*E*)-4-methylhexa-2,4-dienyl acetate and (2*E*,4*Z*)-4-methylhexa-2,4-dienyl acetate (31). Following the general procedure for **30**, 3-methyl-1,3-pentadiene

(**28**) (40 mg, 0.49 mmol), 1,4-diacetoxy-*cis*-2-butene (**12**) (167 mg, 0.97 mmol), and **3** (21 mg, 0.024 mmol) in 1.5 mL CH_2Cl_2 gave 62 mg (82%, >20:1 E/Z) of **31** as a colorless oil. A small amount (9%) of the cross product missing the terminal methyl group was identified by a broad singlet at 5.00 ppm in the ^{1}H NMR spectrum (terminal C=CH_2) and by HRMS (EI) (calc. for $C_8H_{12}O_2$: 140.0837, found 140.0841). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.71 (d, J = 15.5 Hz, 1H, *Z*-isomer), 6.29 (d, J = 15.7 Hz, 1H, *E*-isomer), 5.44-5.77 (m, 2H, both *E*- and *Z*-isomers), 4.64 (d, J = 7.1 Hz, 2H, *Z*-isomer), 4.59 (d, J = 7.4 Hz, 2H, *E*-isomer), 2.06 (s, 3H, *Z*-isomer), 2.05 (s, 3H, *E*-isomer), 1.81 (d, J = 15.9 Hz, 3H, both isomers), 1.72 (s, 3H, *E*-isomer), 1.70 (s, 3H, *Z*-isomer). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) of *E*-isomer: δ 171.1, 139.8, 133.8, 128.8, 119.5, 65.7, 21.2, 14.1, 12.1. HRMS (EI) calc. for $C_9H_{14}O_2$ (for both isomers): 154.0994, found 154.0987 and 154.0994.

Entry 3, (3*E*,5*E*)-5-methylhepta-3,5-dien-2-one and (3*E*,5*Z*)-5-methylhepta-3,5-dien-2-one (32). Following the general procedure for **30**, 3-methyl-1,3-pentadiene (**28**) (40 mg, 0.49 mmol), methylvinylketone (**26**) (34 mg, 0.49 mmol), and **3** (21 mg, 0.024 mmol) in 1.5 mL CH_2Cl_2 gave 42 mg (70%, >20:1 E/Z) of **32** as a colorless oil. A small amount (7%) of the cross product missing the terminal methyl group was identified by a broad singlet at 5.40 ppm in the ^{1}H NMR spectrum (terminal C=CH_2) and by HRMS (EI) (calc. for $C_7H_{10}O$: 110.0732, found 110.0727). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.26 (d, J = 15.7 Hz, 1H, *Z*-isomer), 7.14 (d, J = 15.9 Hz, 1H, *E*-isomer), 6.15 (d, J = 15.9 Hz, 1H, *Z*-isomer), 6.05 (d, J = 15.9 Hz, 1H, *E*-isomer), 6.01 (q, J = 7.1 Hz, 1H, *E*-isomer), 5.88 (q, J = 7.1 Hz, 1H, *Z*-isomer), 2.32 (s, 3H, *Z*-isomer), 2.26 (s, 3H, *E*-isomer), 1.87-

1.90 (m, 3H, *Z*-isomer), 1.83-1.87 (m, 3H, *Z*-isomer), 1.81 (d, J = 7.1 Hz, 3H, *E*-isomer), 1.76 (s, 3H, *E*-isomer). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) of *E*-isomer: δ 199.2, 148.8, 137.7, 134.3, 125.1, 31.8, 27.5, 22.9. HRMS (EI) calc. for $C_8H_{12}O$ (for both isomers): 124.0888, found 124.0882 and 124.0886.

Entry 4, (5*E*,7*E*)-7-propylundeca-5,7-dienyl acetate (33). Following the general procedure for **30**, diene **29** (40 mg, 0.29 mmol), 5-hexenyl acetate (**5**) (165 mg, 1.2 mmol), and **3** (12 mg, 0.014 mmol) in 1.2 mL CH_2Cl_2 gave 56 mg (77%, >20:1 E/Z) of 33 as a colorless oil. The product was not separated from unreacted **5** (1.0:0.32 **33**/**5**). A small amount (12%) of the cross product missing the terminal methyl group was identified by 2 broad singlets at 5.84 and 5.88 ppm in the ^{1}H NMR spectrum (terminal C=C*H*$_2$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.31 (d, J = 15.7 Hz, 1H), 5.64 (dt, J = 15.7, 6.9 Hz, 1H), 5.24 (t, J = 7.1 Hz, 1H), 4.06 (t, J = 6.6 Hz, 2H), 2.06-2.19 (m, 6H), 2.04 (s, 3H), 1.58-1.70 (m, 2H), 1.38-1.52 (m, 6H), 0.89 (q, J = 6.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.4, 136.1, 129.2, 128.7, 127.0, 64.6, 36.5, 33.1, 29.6, 28.3, 26.1, 23.3, 22.2, 21.2, 14.2, 14.0. HRMS (EI) calc. for $C_{16}H_{28}O_2$: 252.2089, found 252.2094.

Entry 5, (2*E*,4*E*)-4-propylocta-2,4-dienyl benzoate (34). Following the general procedure for **30**, diene **29** (40 mg, 0.29 mmol), 1,4-dibenzoyl-2-butene (**27**) (171 mg, 0.58 mmol), and **3** (12 mg, 0.014 mmol) in 1.4 mL CH_2Cl_2 gave 62 mg (79%, >20:1 E/Z) of **34** as a colorless oil. The product was not separated from allyl benzoate formed in the reaction (1.0:0.25 **34**/allyl benzoate). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.05-8.10 (m,

2H), 7.52-7.59 (m, 1H), 7.41-7.48 (m, 2H), 6.70 (dd, J = 15.8, 1.1 Hz, 1H), 5.88 (dt, J = 15.7, 6.3 Hz, 1H), 5.43 (t, J = 7.4 Hz, 1H), 4.91 (dd, J = 6.6, 1.1 Hz, 2H), 2.12-2.21 (m, 4H), 1.35-1.55 (m, 4H), 0.92 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.6, 135.4, 133.1, 132.1, 131.2, 129.8, 128.8, 128.5, 122.2, 66.5, 36.2, 29.7, 23.3, 22.0, 14.2, 14.0. HRMS (EI) calc. for $C_{18}H_{24}O_2$: 272.1776, found 272.1777.

General Procedure for Cross-Metathesis Reactions Using 2-Substituted 1,3-Butadienes (Table 3). Entry 1, (*E*)-4-methylenedec-2-enyl acetate (36). To a solution of **3** (12 mg, 0.014 mmol) in benzene (1.5 mL) was added 1,4-diacetoxy-*cis*-2-butene (**12**) (100 mg, 0.58 mmol) and diene **35** (40 mg, 0.29 mmol). The solution stirred at 60 °C for 12h, and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (5% ethyl acetate:hexanes) to give 44 mg (72%, >20:1 E/Z) of a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.23 (d, J = 16.0 Hz, 1H), 5.70 (dt, J = 15.7, 6.6 Hz, 1H), 4.96 (br s, 1H), 4.94 (br s, 1H), 4.55 (dd, J = 6.3, 1.1 Hz, 2H), 2.11 (t, J = 7.0 Hz, 2H), 2.01 (s, 3H), 1.36-1.43 (m, 2H), 1.18-1.27 (m, 6H), 0.80-0.84 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.0, 145.6, 136.8, 122.4, 116.7, 65.4, 32.0, 31.9, 29.4, 28.2, 22.8, 21.2, 14.3. HRMS (EI) calc. for $C_{13}H_{22}O_2$: 210.1620, found 210.1616.

Entry 2, (*E*)-4-methylenedec-2-enyl benzoate (39). Following the general procedure for **36**, diene **35** (40 mg, 0.29 mmol), 1,4-dibenzoyl-2-butene (**27**) (171 mg, 0.58 mmol), and **3** (12 mg, 0.014 mmol) in 1.4 mL benzene gave 57 mg (73%, >20:1 E/Z) of **39** as a

colorless oil. The product was not separated from allyl benzoate formed in the reaction (1.0:0.46 **39**/allyl benzoate). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.05-8.09 (m, 2H), 7.53-7.60 (m, 1H), 7.44 (t, J = 7.4 Hz, 2H), 6.40 (d, J = 15.7 Hz, 1H), 5.90 (dt, J = 15.9, 6.3 Hz, 1H), 5.06 (br s, 1H), 5.03 (br s, 1H), 4.88 (dd, J = 6.3, 1.1 Hz, 2H), 2.22 (t, J = 6.9 Hz, 2H), 1.45-1.58 (m, 2H), 1.27-1.36 (m, 6H), 0.86-0.91 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.6, 145.6, 136.8, 133.2, 133.1, 129.8, 128.5, 122.6, 116.7, 65.8, 32.1, 31.9, 29.4, 28.2, 22.8, 14.2. HRMS (EI) calc. for $C_{18}H_{24}O_2$: 272.1776, found 272.1778.

Entry 3, (*E*)-4,4,5,5-tetramethyl-2-(3-methylenenon-1-enyl)-1,3,2-dioxaborolane (40). Following a slight modification of the general procedure for **36**, vinyl boronate **23** (89 mg, 0.58 mmol), diene **35**, (40 mg, 0.29 mmol), and **3** (25 mg, 0.029 mmol) in 1.5 mL benzene for 2 h at 60 °C (followed by the same work-up) gave 56 mg (73%, >20:1 E/Z) of a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.03 (d, J = 18.4 Hz, 1H), 5.59 (d, J = 18.4 Hz, 1H), 5.16 (br s, 1H), 5.13 (br s, 1H), 2.20 (t, J = 7.4 Hz, 2H), 1.41-1.48 (m, 2H), 1.20-1.34 (m, 6H), 1.27 (s, 12H), 0.85-0.89 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 152.0, 147.6, 119.3, 83.4, 31.9, 31.5, 29.5, 28.5, 25.0, 22.9, 14.3. HRMS (EI) calc. for $C_{16}H_{29}BO_2$: 264.2261, found 264.2251.

Entry 4, (*E*)-6-(*tert*-butyldimethylsilyloxy)-4-methylenehex-2-enyl benzoate (41). Following the general procedure for **36**, diene **37** (40 mg, 0.19 mmol), 1,4-dibenzoyl-2-butene (**27**) (112 mg, 0.38 mmol), and **3** (8 mg, 0.009 mmol) in 1 mL benzene gave 46 mg (70%, >20:1 E/Z) of **41** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.05-

8.10 (m, 2H), 7.53-7.59 (m, 1H), 7.41-7.47 (m, 2H), 6.39 (d, J = 15.9 Hz, 1H), 5.92 (dt, J = 15.9, 6.3 Hz, 1H), 5.12 (br s, 1H), 5.07 (br s, 1H), 4.88 (d, J = 6.3 Hz, 2H), 3.75 (t, J = 7.1 Hz, 2H), 2.47 (t, J = 7.1 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.5, 142.3, 136.6, 133.2, 130.4, 129.8, 128.5, 122.9, 118.6, 65.7, 62.4, 35.7, 26.1, 18.5, -5.1. HRMS (EI) calc. for $C_{20}H_{31}O_3Si$ [M+H]: 347.2043, found 347.2047.

Entry 5, (*E*)-9-(*tert*-butyldimethylsilyloxy)-7-methylenenon-5-enyl acetate (42). Following the procedure for **36**, diene **37** (40 mg, 0.19 mmol), 5-hexenyl acetate (**5**) (107 mg, 0.75 mmol), and **3** (8 mg, 0.009 mmol) in 1 mL benzene gave 46 mg (75%, >20:1 E/Z) of **42** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.05 (d, J = 15.7 Hz, 1H), 5.69 (dt, J = 15.9, 6.9 Hz, 1H), 4.94 (br s, 1H), 4.88 (br s, 1H), 4.06 (t, J = 6.6 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.43 (t, J = 6.9 Hz, 2H), 2.13 (q, J = 6.9 Hz, 2H), 2.04 (s, 3H), 1.58-1.68 (m, 2H), 1.41-1.51 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.4, 143.0, 132.7, 129.8, 115.3, 64.6, 62.8, 36.0, 32.5, 28.3, 26.2, 25.9, 21.2, 18.6, -5.1. HRMS (EI) calc. for $C_{18}H_{35}O_3Si$ [M+H]: 327.2356, found 327.2366.

Entry 6, (*E*)-*tert*-butyldimethyl(3-methylene-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enyloxy)silane (43). Following a slight modification of the general procedure for **36**, diene **37** (40 mg, 0.19 mmol), vinyl boronate **23** (59 mg, 0.38 mmol), and **3** (16 mg, 0.019 mmol) in 1 mL benzene for 2 h at 60 °C (followed by the same work-up) gave 44 mg (69%, >20:1 E/Z) of **43** as a yellow oil. ^{1}H NMR (300 MHz,

$CDCl_3$, ppm): δ 7.03 (d, J = 18.4 Hz, 1H), 5.60 (d, J = 18.4 Hz, 1H), 5.23 (br s, 1H), 5.18 (br s, 1H), 3.70 (t, J = 7.1 Hz, 2H), 2.46 (dt, J = 7.1, 1.1 Hz, 2H), 1.27 (s, 12H), 0.87 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 151.8, 144.1, 121.0, 83.4, 62.4, 35.0, 26.1, 25.0, 18.5, -5.1. HRMS (EI) calc. for $C_{18}H_{35}BO_3Si$: 338.2449, found 338.2455.

Entry 7, (*E*)-*tert*-butyldimethyl(2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enyloxy)silane (44). Following a slight modification of the general procedure for **36**, diene **38** (40 mg, 0.20 mmol), vinyl boronate **23** (62 mg, 0.40 mmol), and **3** (17 mg, 0.020) in 1 mL benzene for 2 h at 60 °C (followed by the same work-up) gave 37 mg (approximately 73% pure; ~40% yield based on impurities and unreacted, inseparable boronate **23**, >20:1 E/Z) of impure **44** as a yellow oil. Peaks given in spectral data are only those corresponding to **44**. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.06 (d, J = 18.9 Hz, 1H), 5.49 (q, J = 1.9 Hz, 1H), 5.48 (d, J = 18.7 Hz, 1H), 5.28 (br s, 1H), 4.36 (t, J = 1.6 Hz, 2H), 1.28 (s, 12H), 0.92 (s, 9H), 0.07 (s, 6H).

Entry 8, (*E*)-4-((*tert*-butyldimethylsilyloxy)methyl)penta-2,4-dienyl benzoate (45). Following the general procedure for **36**, diene **38** (40 mg, 0.20 mmol), 1,4-dibenzoyl-2-butene (**27**) (119 mg, 0.40), and **3** (9 mg, 0.01 mmol) in 1 mL benzene gave 42 mg (63%, >20:1 E/Z) of **45** as a pale yellow oil. Compound **45** was not separated from allyl benzoate formed in the reaction (1.0:0.55 **45**:allyl benzoate). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.03-8.09 (m, 2H), 7.53-7.59 (m, 1H), 7.44 (t, J = 8.0 Hz, 2H), 6.40 (d, J = 15.9 Hz, 1H), 5.87 (dt, J = 15.9, 6.3 Hz, 1H), 5.37 (br s, 1H), 5.17 (br s, 1H), 4.86 (d, J

= 6.3 Hz, 2H), 4.35 (s, 2H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.5, 144.0, 134.0, 133.2, 129.8, 128.5, 122.7, 118.4, 116.1, 65.8, 62.9, 26.1, 18.5, −5.2. HRMS (EI) calc. for $C_{19}H_{29}O_3Si$ [M+H]: 333.1886, found 333.1888.

(*E*)-1-(3-methylpenta-1,3-dienyl)benzene (46). To a solution of **3** (14 mg, 0.016 mmol) in benzene (1.5 mL) was added vinylboronate **23** (50 mg, 0.32 mmol) and diene **28** (26 mg, 0.32 mmol), and the solution stirred at 40 °C for 2.5 h. The reaction solution was cooled to rt, and $Pd(PPh_3)_4$ (11 mg, 0.0097 mmol), bromobenzene (50 mg, 0.32 mmol), and NaOEt (2M in EtOH, 0.46 mL, 0.91 mmol) were added. The solution stirred at 80 °C for 5 h. The reaction mixture was purified by flash chromatography (100% hexanes) to give 23 mg (45%) of **46** as a colorless oil. A small amount (13%) of the cross product missing the terminal methyl group was identified by two broad singlets at 5.09 ppm and 5.14 ppm in the ^{1}H NMR spectrum (terminal C=CH_2). Characterization data matched that in the literature.[vii] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.41-7.48 (m, 2H, both *E*- and *Z*-isomers), 7.28-7.36 (m, 2H, both *E*- and *Z*-isomers), 7.18-7.26 (m, 1H, both *E*- and *Z*-isomers), 6.90 (d, J = 16.2 Hz, 1H, *Z*-isomer), 6.83 (d, J = 16.2 Hz, 1H, *E*-isomer), 6.57 (d, J = 15.9 Hz, 1H, *Z*-isomer), 6.46 (d, J = 15.9 Hz, 1H, *E*-isomer), 5.73 (q, J = 7.1 Hz, 1H, *E*-isomer), 5.56 (q, J = 7.1 Hz, 1H, *Z*-isomer), 1.95 (m, 3H, *Z*-isomer), 1.88 (t, J = 1.1 Hz, 3H, *E*-isomer), 1.82 (d, J = 7.1 Hz, 3H, *E*-isomer); terminal methyl resonance of *Z*-isomer overlaps with those of the major isomer.

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